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Impacts of biodiesel combustion on NO_x emissions and their reduction approaches

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ABSTRACT

Increasing energy demand and environment concerns have prompted an evolution of alternative fuel sources. As an alternative fuel source, biodiesel is attractive because it reduces engine emissions. However, biodiesel produces higher NO_x emissions compared to ordinary diesel fuel. Previous researches have established many factors that cause biodiesel to produce elevated NO_x emissions. This study reviews the impacts of biodiesel combustion on NO_x emissions and their reduction approaches in diesel engines. The first part of this study recaps the NO_x formation mechanisms for understanding the kinetics behind the NO_x forming reactions. The second part describes the factors affecting on NO_x emissions. This paper established that higher NO_x emissions are produced for biodiesel combustion which influenced by several factors such as physicochemical properties and molecular structure of biodiesel, adiabatic flame temperature, ignition delay time, injection timing and engine load conditions etc. The final section discusses on the reduction of NO_x emissions from biodiesel fuelled engines for both pre and post combustion techniques. The results of reduction approaches of the NO_x emissions implies, exhaust gas recirculation (EGR) and retarded injection timing are effective as well as low cost techniques than others. Between these two techniques, EGR reduces the NO_x emissions at 5–25% EGR rate adequately in biofuelled engine by controlling oxygen content and combustion peak temperature with slightly decreasing HC and CO emissions. However this technique shows few penalties on smoke and PM emissions as well as brake specific fuel consumption if not perfectly optimized.

Contents

Abbreviations: NO_x, oxides of nitrogen (NO, NO_2); HC, Hydrocarbon; CO, carbon monoxide; PM, particulate matter; T_{ad}, adiabatic flame temperature; NHD, *n*-hexadecane; HMN, 2,2,4,4,6,8,8-heptamethylnonane; CN45, 35.3 vol% NHD with balance HMN; CN70, 64.7 vol% NHD with balance HMN; CN45, 35.3 vol% NHD with balance HMN; IMEP, indicating mean effective pressure; SOI, start of injection; Φ, stoichiometric air fuel mixture; BSFC, brake specific fuel consumption; BTE, Brake thermal efficiency; FAME, fatty acid methyl ester; JME, jatropha oil methyl ester; JOME, jojoba oil methyl ester; SME, soybean oil methyl ester; SOME, sunflower oil methyl ester; WOME, waste cooking oil methyl ester; CSOME, cottonseed oil methyl ester; COME, corn oil methyl ester; CME, canola oil methyl ester; NOME, neem oil methyl ester; ROME, rapeseed oil methyl ester; TOME, tall oil methyl ester; CNOME, coconut oil methyl ester; TPOME, thevetia peruviana oil methyl ester.

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1. Introduction

Petroleum-based fuels play a very significant role in the fields of industrial growth, transportation, agriculture, etc., due to their availability, combustion properties and high heating value. However, the reserves of these fuels are rapidly depleting due to increased fuel consumption. According to the estimation of the International Energy Agency, by 2030 global energy consumption will be increased about 53% [1,2]. The United States Energy Information Administration (EIA) has projected that the world's liquid fuel consumption will increase from 86.1 million barrels/ day, to 110.6 million barrels/day by 2035 [3,4]. The emissions caused by the burning of petroleum-derived fuels have a serious effect on both the environment as well as human health. Fossil fuel depletion, increasing the price of fossil fuel and global environmental concerns have generated more interest in alternative, environmentally friendly sources of fuel. Therefore, it has become a global agenda to develop clean alternative fuels that are domestically available, environmentally acceptable, and technically feasible. Biodiesel is considered as a better choice of alternative fuel due to its environmentally friendly characteristics and similar functional properties of diesel fuel. Biodiesel has an immense potential to be part of the future energy mix. In developing countries, using biodiesel in internal combustion engines can play an important role in reducing the fossil fuel demand, the environmental impact, and the adverse effects on human health [5]. Biodiesel is renewable and can be produced directly from edible and non-edible vegetable oils, recycled waste vegetable oils, and animal fats through the transesterification process [2]. Generally, biodiesel fuels offer reduction of harmful pollutant emissions such as CO, HC and PM, but it produces higher NO_x emissions [6–16]. The NO_x emissions are the most harmful parameters that affect the environment through acid rain, human disease, etc. Furthermore, CO and NO are primary pollutants in the formation of tropospheric ozone, which is an important greenhouse gas [17]. The United States Environmental Protection Agency (EPA) estimated an average 10% increase in NO_x emissions for a pure (100%) biodiesel fuel compared to conventional diesel fuel [4,18]. Wu et al. [19] found that the reduction of exhaust emissions fuelled with five types of biodiesel individually as a range such as PM, dry soot, HC and CO to be about 53–69%, 79–83%, 45–67%, 4–16%, respectively, but an increase in NO_x of 10–23% compared with petroleum diesel. Very few authors have found reduced the NO_x emissions for biodiesel fuels combustion [20–22]. Sun et al. [10] reported that biodiesel fuel gives higher NO_x due to: the advancement of injection timing, the higher T_{ad}, less radiative heat transfer, increase in ignition delay, higher degree of unsaturation, and high oxygen content, etc. As use of biodiesel in diesel engine has increased tremendously, higher NO_x emissions could become a significant barrier to its spread in the market. Therefore researchers are persistently looking for a reliable and economically viable solution to this problem. Some of them have already managed to establish some techniques. This will help end users to overcome the problem of biodiesel expansion.

Many researchers have examined the combined analysis of the effect of biodiesel combustion on engine performance and emissions; and reduction of the NO_x emissions but few of them attempted to review them [23,24]. This paper presents a comprehensive review on the effects biodiesel combustion on NO_x emissions of biodiesel fuelled engines, in order to provide useful information to engineers, policy makers, industrialists and researchers. Articles from highly rated journals as well as SAE technical papers are reviewed to discuss the notable factors affecting NO_x emissions of biodiesel fuel. Finally, reduction techniques of the NO_x emissions (both pre and post combustion) are described for biodiesel fuelled engine.

2. NO_x formation mechanisms

Nitrogen oxide is the generalized term for NO and NO_2 given with the formulae of NO_x [25]. Understanding the kinetics behind the NO_x forming reaction is important for taking attempt to reduce the NO_x emissions. The thermal (Zeldovich), prompt (Fenimore), N_2O pathway, fuel-bound nitrogen and the NNH mechanism are the most common mechanisms for NO formation in diesel combustion [26]. Among them thermal and prompt are the dominant mechanisms of NO_x formation in biodiesel combustion [27]. The atmospheric or molecular nitrogen is the main source of nitrogen for NO_x formation during conventional combustion of typical petroleum and bio-based fuels. Based on literatures, the general NO_x formation mechanisms are summarized below [10,23,28–32].

2.1. *Zeldovich mechanism*

NO_x formation occurs at temperature above 1700 K by this mechanism [23]. At this temperature nitrogen (N_2) and oxygen

(O_2) react through a series of chemical steps known as Zeldovich mechanism. The rate of formation increases rapidly with temperature. This mechanism of thermal NO_x formation is believed to be the predominant contributor of total NO_x. The basic kinetic equations for thermal NO_x formation are described by the following chemical reactions (1)–(3).

$$N_2+O\leftrightarrow NO+N \tag{1}$$

$$N+O_2\leftrightarrow NO+O \tag{2}$$

$$N+OH\leftrightarrow NO+H \tag{3}$$

The first step is rate limiting, and due to its high activation energy (314 kJ/mole), requires high temperatures to proceed. Reaction (3) is only significant under reducing conditions. Residence time and the concentration of nitrogen and oxygen also have an influence on the production of thermal NO [28]. Hu and Huang [33] theoretically proved that NO_x formation depends directly on two factors: the concentration of reactants, and temperature.

2.2. Prompt or Fenimore mechanism

The presence of a second mechanism leading to NO_x formation was first identified by Fenimore and was termed “prompt NO_x”. There is a good evidence that prompt NO_x can be formed in a significant quantity in some combustion environments; such as in low-temperature, fuel rich conditions and where residence time is short [32,34]. Prompt NO_x is most prevalent in rich flames. The actual formation involves a comply series of reactions and many possible intermediate species. Prompt NO_x is produced when hydrocarbon fragments react with nitrogen in the combustion chamber to form fixed nitrogen species such as HCN [35]. After that these nitrogen-containing fragments react with atmospheric nitrogen. Prompt NO_x is more sensitive than thermal NO_x in fuel chemistry because of the dependence on hydrocarbon fragments. Miller and Bowman [36] studied the mechanism and modeling of nitrogen chemistry in combustion and stated that in order to estimate the total NO_x, the prompt NO_x must be considered, which was also verified by the recent study by Ren and Li [37]. The prompt NO_x is generally formed through the following reactions (4) to (8).

$$CH+N_2\leftrightarrow HCN+N \tag{4}$$

$$CH_2+N_2\leftrightarrow HCN+NH \tag{5}$$

$$N+O_2\leftrightarrow NO+O \tag{6}$$

$$HCN+OH\leftrightarrow CN+H_2O \tag{7}$$

$$CN+O_2\leftrightarrow NO+CO \tag{8}$$

Here, CH and CH_2 are the significant contributors to form prompt NO_x (Eqs. (4) and (5)). The formation of prompt NO_x is proportional to the number of carbon atoms in each unit volume. Prompt NO_x is independent of the parent hydrocarbon. The amount of HCN increases with increasing the concentration of hydrocarbon radicals which enhances with increasing equivalence ratio. Prompt NO_x formation increases with an increasing equivalence ratio and then reaches a peak and decreases because of a shortage of oxygen.

2.3. Fuel NO_x mechanism

Fuel NO_x is formed when nitrogen that is chemically bound in the fuel combines with excess oxygen during the combustion process. The type of NO_x is negligible for both diesel and biodiesel because of low nitrogen levels [23]. Biodiesel has an average nitrogen concentration of only 0.02% [35]. Addition of additives containing nitrogen atoms e.g. pyridine, pyrrole etc. may lead to more fuel NO_x formation. This can be attributed to weaker C–N bond compared to N–N bond. The C–N bond in pyridine and pyrrole are shown in Fig. 1. The main pathway for this type of NO_x formation involves the creation of intermediate nitrogen containing species such as HCN, NH_3, NH, or CN. These molecules can then be oxidized to form NO_x [34].

2.4. N_2O pathway mechanism

The NO_x formation due to the N_2O pathway is another essential mechanism in a combustion process under high pressure and lean air-fuel ratio compared with Fenimore NO, and a minor contribution to the formation of NO_x related to the thermal NO mechanism [38]. In this mechanism, the reaction occurs between N_2 and atomic oxygen to form N_2O by a three-body reaction.

$$O+N_2+M\leftrightarrow N_2O+M \tag{9}$$

Here, the molecule M is required to execute this reaction. The N_2O formed in reaction (9) can then react to form NO which is shown in Eq. (10).

$$N_2O+O\leftrightarrow NO+NO \tag{10}$$

2.5. The NNH mechanism

Under the condition of high concentration of atoms in fronts of flame in combustion process the reaction (Eq. (11)) contributes significantly to produce NO.

$$O+NNH\leftrightarrow NO+NH \tag{11}$$

The mechanism requires the participation of H atoms to form NNH (diazanul) from N_2, as well as O atoms to react with NNH [26].

3. Factors affecting NO_x emissions

Many researchers have proposed many possible reasons for the increase of NO_x emissions when biodiesel is used in diesel engine [10,23,28]. Summarizing of the review on factors affecting biodiesel NO_x as well as other criteria emissions is presented in Table 1. On the other hand few of them also found reduced NO_x emissions using biodiesel fuels [39,40]. They have also proposed other mechanisms. No single factor is responsible for these NO_x effects. However the exact cause is still under investigation. The possible causes that have been proposed by the researchers to explain the biodiesel NO_x increase are presented in this section.

3.1. Physicochemical properties of biodiesel

The physical and chemical properties of biodiesel such as: viscosity, density, bulk modulus of compressibility, sound velocity, cetane number, iodine value, surface tension, thermal conductiv-

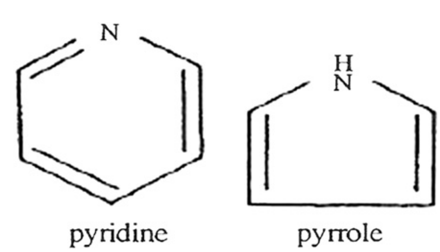


Fig. 1. Organic, fuel bound nitrogen compounds in solid fuels.

Table 1
Summarizing the review on factors affecting biodiesel NO_x as well as other criteria emissions.

Fuel	Engine used & condition	Results compared to diesel fuel (%)		Explanation for higher NO_x	*Source*
		NO_x	Others emission		
POME25 POME50 POME75 POME100	IRLOSKAR TV-1, 1C, DI, NA, WC, DE, Max power output: 5.2 kW, IT 23.51bTDC CR 17.5 IP: 19.6 MP, full load, CS = 1500 rpm	↑ high ↑ less ↑ less ↑ less	CO↓21.4, HC↑9.52, Smoke↑9.8, CO↓35.2, HC↓9.53 CO↓35.2, HC↓19.05, Smoke↓10, CO↓52.9, HC↓38.09, Smoke↓19,	Fuel burn during the late phase of combustion resulting in higher exhaust temperature because of having higher molecular weights.	[41]
POME20 POME50	3C, 2.5L Perkins AD 3–152 Max engine power of 44 kW at 2132 rpm, 8-mode cycle	Max ↑24 ↑(0.32 –25)	CO↓20(avg.) CO↓27(avg.)	The higher the number of double bounds in the biodiesel molecular structure.	[42]
ROME100	Lister Petter 1C, DI, CR 15.5, Max power 8.6 kW at 2500 rpm, CS = 1500 rpm, VL: 2 bar, 4 bar and 5 bar EGR variation at each load: 0 and 30%	↑(7–11)	CO↓, HC↓23 (0% EGR) & HC↓41 (30% EGR), smoke(BSN)↓52, PM↑ with↑load,	The higher cylinder pressures, injection timing advance and high amount of fuel injection.	[43]
ROME100	MAN D2566 MUM 6C, bus engine, CR 17.5 Mechanically controlled DI, Max power 162 kW at 2200 rpm	↑	CO↓, HC↑, Smoke↓ & (-) (CO, HC & smoke) with (+) speed for both fuel	Higher oxygen content into biodiesel fuel	[44]
ROME80 ROME100	Juling SD-1110 1C, CR 16.5, Rated power 20 HP (14.7 kW)	↑(4.17 ± 0.1) ↑(6.27 ± 0.2)	CO↓(32.47 ± 0.4), PM↓(27.7 ± 1.6) CO↓ (30.57 ± 1.1), PM↓(39.8 ± 2.0)	Biodiesel has low sulphur content and presence of high fuel bound oxygen.	[40]
ROME50	4C, 46 kW DI, CR 16.1 Max power 46 kW at 2400 rpm, full load, speed+(1200–2100) rpm	↑7.82 (avg.)	CO↓15.53, CO_2↑ 2.9, smoke ↓46.29	The high oxygen content and higher density of ROME fuel results higher combustion temperature	[45]
WOME5, WOME10, WOME20, WOME30	Cummins B5.9–160, DI, IP = 250 bar, IT = 12.3 BTDC CR: 17.9: 1, max. power 118 kW at 2500 rpm, a max. torque of 534 N/m at 1600 rpm	↑(0.73–2.19)	CO↓(3.33–13.1), HC↓(10.5–36.0), CO_2↑(0.117–1.06), PM↓(5.29–8.53), PAHs↓(7.53–37.5)	Not mention	[46]
WOME25, WOME50, WOME75	MWMD229/4, 50 kW, NA, 4S, 4C, mechanically controlled DI fuel system, VL = 0 to 25 kW,	↑7.1(WCB25), ↑4.8(WCB50), ↑6.5(WCB75), Max variation occurred at LL	CO↑19.2(WCB25), ↑20.1 (WCB50),↑46.1(WCB75);HC↑0.6 (WCB25),↑23.5 (WCB50); CO_2↑5.3 (WCB25), ↑8.5(WCB50),↑13.3 (WCB75), Max variation occurred at HL	NO_x increases with increasing engine load, cylinder pressure and temperature are increased as a result of larger fuel amount being burned in the combustion chamber.	[47]
SME5 SME20 SME50 SME100	4S, NA, 4C,DI diesel engine, 1600 rpm, full load	same ↑8.26 ↑10.5 ↑18.34	CO↓2.8, smoke↓6.6 CO↓8.5, smoke↓19.6 CO↓18.4, smoke↓31.28 CO↓32.1, smoke↓54.5	Higher oxygen content and lower calorific value of SME fuel.	[48]
SME100	Yanmar L100V, vertical DI, CI Engine, NA, AC, 4S, 1C, rated power 6.2 kW at 3600 rpm	↑56 (LL) ↓4 (ML) ↓20 (HL)	CO↓8(LL) ↓34 (ML) ↓27 (HL), HC↓64 (LL) ↓14(ML) ↓2.5 (HL), PM↓56 (after 1 h test)	–	[4]
JME5, JME10, JME20, JME50 & JME100	3.3-L 4C, DI, TC, intercooled, HPCRS, Rated power output 79 kW at 3200 rpm, VL: 10%, 25%, 50% & 75% full load, CS: 2000 rpm	↑(1.02, 2.06, 4.74, 5.71 & 13.9 with increasing JME blends at HL)	(CO↑ at LL, CO↓ at HL, smoke↓4.54 for JME5); (CO↑ at LL, CO↓ at HL, smoke↓14.1 avg. for JME10); (CO↑ at LL, CO↓ at HL, smoke↓24.9 avg. for JME20); (CO↑ at LL, CO↓ at HL, smoke↓54.0 avg. for JME50) & CO↑(2.3–17.6) at LL, CO↓ (15–23.1) at HL, HC↓(26.5–27.6) at LL, HC↓(30.9–46.7) at HL, smoke↓80.5(avg.) for JME100	The higher bulk modulus and sound velocity and viscosity, lead to an advanced start of injection. This, jointly with any cetane number increase, may slightly advance the start of combustion.	[49]

JME5, JME10, JME20, JME30, JME100,	Kirloskar 1C, AC, DI, NA diesel engine, VL: 0%, 20%, 40%, 60%, 80% & 100% load	NO_x↑ with ↑(load and blend ratio)	CO↓ with ↑blend ratio, CO_2↑ with ↑(blend ratio and load), HC↓ with ↑(blend ratio and load), smoke↓	The shorter ignition delay and the increased amount of biodiesel undergoing premixed combustion results in higher cylinder pressure and hence temperature.	[13]
JME5, JME10, JME20, JME30, JME40 & JME50	Kirloskar 1C, DI, AC diesel engine CR 17.5 speed 1500 rpm rated power 4.4 kW IP=200 bar, Variable load	NO_x↑ with↑load	CO↓ with↑blend ratio, Smoke↑ with ↑(load and blend ratio)	The higher exhaust gas temperature is an important cause for biodiesel higher NO_x	[50]
JME5 JME10	Yanmar 1C, NA Engine CR 17.7 Max. Power 7.7 kW IT 171 BDTC, CS: 2300 rpm, Throttle position (TP): 100% and 80%	↑(4–9.5) ↑(6.25–17)	CO↓(17.26–20.7), HC↓(8.96–16.28) CO↓(25.92–33.24), HC↓(11.25–30.23)	Higher fuel borne oxygen and higher burned gas temperature	[51]
Rice bran biodiesel (RBB100)	Kirloskar model AV1, 4S, 1C,Vertical, WC, CR:16.5:1, Rated power 3.72 kW	↑4 (NO_x↑ with↑engine load)	CO↓25.8, CO_2↑, HC↓54, smoke↑27.93; all emission increases with↑engine load	Higher combustion temperature as well as the O_2 content of the biodiesel fuel	[52]
TPOME100	1C, CR=16.5:1, Rated power=3.7 kW, Rated speed=1500 rpm, full load	↑9.44	CO↓12.5, HC↓8.75, smoke↑8.5	Higher exhaust gas temperature due to heavier molecules of biodiesel	[53]

Note: ↑indicates increase,↓indicates reduced, HPCRS=High-pressure common rail fuel system.

ity, chain length, heat capacity and fuel composition etc. have a significant effect on NO_x emissions. The Physicochemical properties of diesel and some commonly used biodiesel fuels are presented in Table 2.

Fuel viscosity has significant effect on NO_x emissions. Anderson and Olsen [54] analyzed NO_x emissions as a function of viscosity and found an increase in NO_x with increasing viscosity at low temperatures. Generally the kinematic viscosity of biodiesel is greater than that of diesel fuel (Table 2), which reduces fuel leakage during injection and leads to increased pressure as well as advanced injection timing [55]. The advance in injection timing facilitates increased fuel mass injected which in turn results in increased NO_x emissions. Moreover, Yuan and Hansen [56] observed reduced NO_x emissions of about 3.52% with reduced viscosity of soy methyl ester to a level of petroleum diesel fuel.

The NO_x emissions increase with increasing fuel density as well as decreasing cetane number (CN) [29,57,58]. The start of injection (SOI), the injection pressure, and the fuel spray characteristics are affected by the fuel density, which influences combustion as well as emissions. In modern diesel engine, fuel injection systems measure the fuel by volume. As a result, the changes in the fuel density will greatly act upon mass of fuel injected and corresponding NO_x emissions [57]. Moreover Boehman et al. [59] found the relationships between FAME density and NO_x emissions as increased NO_x emissions with increasing FAME density.

Tat et al. [60] reported that, vegetable oils and their methyl esters are less compressible and have greater speed of sound, which means they have a higher bulk modulus of compressibility than diesel fuel. As a result, the fuel injection pressure develops faster and the fuel is injected sooner. Earlier start of injection delivers increased fuel mass delivery in most engines. Combustion of higher quantity mass develops an elevated temperature, which causes more NO_x formation. Tat and Van Gerpen [61] studied the effect of fuel property changes on injection timing and finally reported advanced injection timing of about 1° due to the high value of bulk modulus and the speed of sound which may be partially responsible for increasing the NO_x emissions. It was also found that 60 vol% blend of biodiesel and a paraffinic solvent (Norpar-13) displays the same bulk modulus of compressibility as a diesel fuel [59]. Hence, one scheme for combating the “biodiesel NO_x effect” is to use highly paraffinic diesel fuels, such as F–T diesel as the diesel base stock.

The higher cetane number of biodiesel implies shorter ignition delay which reduces the combustion temperature as well as residence time, consequently less NO_x formation [62,63]. In general, higher saturated fatty acids biodiesel such as coconut, palm and tallow shown in Table 3, produce less NO_x than mineral diesel and have a higher cetane number [64,65]. Despite of having a high cetane number, it produces higher NO_x than diesel fuel usually. Wang et al. [66] gave suggestion of this regard that, high CN of biodiesel tend to increase peak pressure and temperature due to shortened ignition delay which leads to enhanced NO_x formation. Mueller et al. [67] also investigated the biodiesel NO_x effect and reported that somewhat higher cetane number of biodiesel relative to diesel causes ignition to occur earlier in the cycle. This allows the combustion products to have a longer residence time at high temperatures, which increases NO_x emissions.

The Iodine value (IV) of biodiesel directly impacts on NO_x emissions. The emissions of NO_x increase with an increasing iodine value of biodiesel, which was investigated by McCormick et al. [58]. The measurement of the degree of unsaturation of fatty acid is indicative of the iodine value. Thus, a higher degree of unsaturation indicates a higher iodine value. Wyatt et al. [68] carried on emission tests with the TOME (IV: 53.6), lard methyl ester (IV: 62.5) and chicken fat esters (IV: 77.4) and compared with SOME (IV: 129.1) and found that NO_x emissions are linearly correlated

Table 2
Properties of diesel and different biodiesel fuel.

Properties fuel name	Calorific value (kJ/kg)	Density (kg/ m^3)	Iodine value (IV)	Cetane number	Kinematic viscosity at mm^2/s		O_2 content (% weight)	References
					27 °C	40 °C		
Diesel fuel	43,350	815	–	47.0	4.3	–	0	[73–79]
SOME	40,579	878	110–143	37.1–51	10	4.22	10.89	[28,73,80–86]
CSOME	40,580	874	90–140	41.8–51.2	11	4–6.1	10.49	[28,80,87–90]
SME	39,760	872	117–143	38–46.2	11	4.08	10.92	[28,80,82,88]
WOME	40,055	870		56			11.3	[19]
COME	41,140	873–913	103–140	37.6	–	3.62	10.96	[73,80,82,91]
ROME	41,550	857–914	94–120	37.6–54.4	–	4.6–6.7	10.9	[28,73,80,91,92]
POME	41,240	867	44–54	42–62		5–6	11.27	[28,73,87,91,93]
KOME	38,300	875	81	55.84		3.99–4.2	11	[63,94]
JME	38,450	880	109.5	50.0–54.0		4.75–5.65		[73,81,95]

Table 3
Typical fatty acid (FA) groups with composition in biodiesel. *Source*: [72,81,87,96,97].

Common name	Formal name	C:N	Molecular formula	FAME composition (EN14103) (m/m %) for different biodiesel								
				ROME	POME	JME	Tallow	CNOME	SME	SOME	Peanut	CME
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$	0.0	0.2	0.0	0.1	45.6	–			
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$	0.1	1.1	0.0	3.3	22.1	0.1	0.1		0.1
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$	4.6	43.0	12.6	25.2	10.2	10.3	6.0	10.4	3.9
Palmitoleic acid	cis-9-hexadecanoic acid	16:1	$C_{16}H_{30}O_2$	0.3	0.2	0.8		–				
Stearic acid	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$	1.8	4.7	5.9	19.2	3.6	4.7	5.9	8.5	3.1
Oleic acid	cis-9-octadecenoic acid	18:1	$C_{18}H_{34}O_2$	60.7	40.1	35.8	48.9	8.2	22.3	20.43	47.1	60.2
Linoleic acid	cis-9,12-octadecadienoic acid	18:2	$C_{18}H_{32}O_2$	19.1	9.5	28.8	2.7	2.7	54.1	66.2	32.9	21.1
Linolenic acid	cis-9,12,15-octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$	8.3	0.2	0.2	0.5	0.0	8.3	0.6	0.5	11.1
Others				5.1	1.0	15.9	0.1	7.6	0.2		0.6	0.5
Saturated fatty acids (%)				6.5	50.2	18.5	47.8	81.5	37.4	32.43	66	67.3
Unsaturated fatty acids (%)				88.4	48.8	65.6	52.1	10.9	62.6	67.57	34	32.7

Note: C:N, C the number of carbons and N the number of double bonds of carbons in the fatty acid chain.

Table 4
T_{ad}, at constant pressure, stoichiometric mixture for the different fuel by using software GASEQ, *Source*: Glaude et al. [72].

Fuel condition	DF1 (C/H) 0.537	DF2 (C/H) 0.555	DF3 (C/H) 0.671	ROME	SOME	SME	POME	TOME	Naphtas (C/H) 0.476	Naphtas (C/H) 0.515	Natural Gas (Alaska)	Natural Gas (Libya)
Case: 1	2291	2292	2309	2287	2291	2290	2279	2278	2281	2287	2227	2245
Case: 2	2560	2560	2578	2556	2559	2558	2547	2546	2548	2553	2449	2509
Case: 3	2523	2523	2541	2519	2522	2521	2510	2509	2511	2517	2454	2470

Note: Case1: $T=300$ K, $P=1$ atm; case 2: $T=673$ K, $P=13$ atm; case 3: $T=623$ K, $P=11.5$ atm.

with an IV of fatty acid ester. Moreover, Peterson et al. [69] conducted emission tests with several FAME fuels and reported that with increase in IV from 7.88 to 129.5, the NO_x emissions were raised by 29.3%.

The NO_x concentration is considered as a strong function of fuel surface tension [71]. It has been found that the increase in surface tension will result in increases in NO_x emissions. According to [28], the surface tension of biodiesel is 22% higher compared to diesel. Diesel spray properties, specifically the droplet size distribution and Sauter mean diameter (SMD), are influenced by fuel surface tension and viscosity. The SMD has been found to increase with increasing surface tension and viscosity. The SMD of biodiesel fuels varies from 5 to 40% higher than diesel fuel. Moreover, the increased droplet size can reduce the fraction of fuel burned in the premixed combustion phase and lead to increased duration of diffusion flame combustion [70]. Hence increases the NO_x concentration.

Other physical properties of biodiesel such as liquid thermal conductivity, radiative heat loss and vapor heat capacity are slightly lower than diesel fuel which allows to rise its temperature at a faster rate once injected, resulting in evaporated droplets sooner than petroleum diesel. Sun et al. [10] reported that biodiesel combustion inside cylinder has less radiative heat transfer due to less soot formation which can be ascribed as a cause of NO_x emissions. So variations of these properties have significant influences on NO_x formation rate.

3.2. Adiabatic flame temperature

Ban-Weiss et al. [29] reported that unsaturated molecules show higher T_{ad} than their saturated counterparts based on combustion of model compounds. Theoretically it can be said that biodiesel gives higher flame temperature than conventional diesel because of having a higher concentration of unsaturated compounds. The increased thermal NO_x formation would be expected due to higher flame temperature. However, there is little experimental evidence to suggest that changes in T_{ad} when using biodiesel is a major contributor to the observed NO_x effect [67]. Moreover, Glaude et al.

[72] identified the effect of T_{ad} on NO_x for biofuels and fossil fuels. The synopsis of this deduction is that for biodiesel fuel, gas turbine emits slight less NO_x compared to diesel due to lower T_{ad} shown in Table 4.

3.3. High oxygen content

Biodiesel is an oxygenated fuel and it contains oxygen of about 11% by weight [28,98]. Several scientists [6–14,16,19,99,100] have investigated the effects of biodiesel fuel on exhaust emissions, and found a significant reduction in CO, sulfur, smoke, PM, and noise emissions. They explained these attributing to the high oxygen content leading to complete combustion. The presence of oxygen in biodiesel fuel results in higher heat release during the premixed phase combustion. Rapid breakage of hydrocarbon contributes to a hotter combustion process, which can be regarded as the main contributor to increased NO_x emissions [67,101]. Nabi et al. [102] tested a four-stroke diesel engine with KOME biodiesel and observed that NO_x increased by about 15% under high load conditions, because of the 12% oxygen content of B100, which resulted in a higher gas temperature in the combustion chamber. Lin et al. [82] observed a comparison of eight kinds of vegetable oil methyl ester (VOME) fuels in diesel engines and showed that every biodiesel fuel emits more NO_x compared to diesel fuel, within a range from 5.58% to 25.97%. Rao et al. [94] concluded in their article that due to the 11% oxygen content in KOME fuel, NO_x emissions were higher. They reported that the oxidation of nitrogen is improved with the presence of more oxygen in KOME fuel, which raised the combustion bulk temperature during the combustion period. In contrast, Lapuerta et al. [86] inferred that the oxygen content of biodiesel could not be the cause for an increase in NO_x because the oxygen/fuel mass ratio of biodiesel (2.81) is less than that of the diesel (3.58). Lapuerta et al. [76] also showed that there was no significant difference between the diesel and biodiesel NO_x emissions. They tested different blends of waste cooking oil methyl and ethyl esters in a 2.2 L, CRDI diesel engine and found a very slight difference in NO_x emissions between the biodiesel and diesel fuel.

In contrast, some researchers [20–22] reported that the oxygenated biodiesel produced less NO_x emissions than diesel fuel. Nabi [21] found from his theoretical investigation that the T_{ad} decreases due to an increase in the oxygen content of the oxygenated fuels, and as a result, NO_x emissions decrease linearly, which is shown in Fig. 2. He showed that indicated thermal efficiency mostly depends on the oxygen content of the oxygenated fuels, and is almost constant at oxygen content below 30% w/w, but decreases

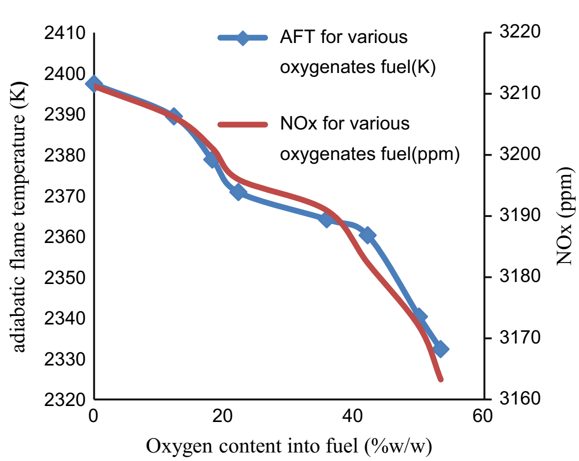


Fig. 2. Adiabatic flame temperature (T_{ad}) and NO_x emissions with Pentadecane and different oxygenated fuel ($\varphi = 1.0$) [21].

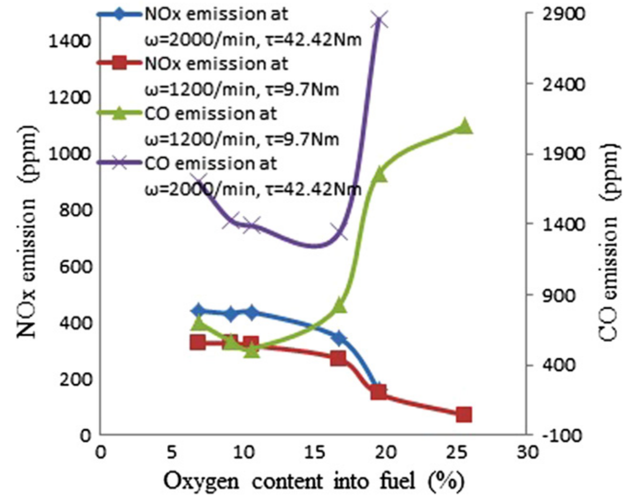


Fig. 3. Effect of fuel oxygen content on NO_x and CO emission [22].

gradually with the increase in oxygen content above 30% w/w. Furthermore, it was observed that due to the higher oxygen content, viscosity, density, and lower calorific value, the T_{ad} decreases, as reported by Gongping et al. [20]. Sendzikiene et al. [22] tested a single-cylinder direct injection AVL test engine with tri-component (ROME-D-E) fuel and found that the optimum oxygen content in the mixture of this tri fuel is 15–19% considering performance and emissions. Fig. 3 shows that if the oxygen content in the (ROME-D-E) fuel mixture is more than 19%, NO_x emissions decrease, but rapidly increases the CO for two given conditions. This is why it is necessary to minimize the oxygen content in the fuel to obtain the optimum results of engine performance and emissions for oxygenated fuel.

3.4. Molecular structure of biodiesel fuel

Many researchers [25,81,103] observed that, the biodiesel molecular structure has a substantial impact on combustion and hence emissions. The structural formula and fatty acid composition of some biodiesel fuels are presented in Table 3. Shahabuddin et al. [97] reported that the cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation of the FAME molecule. Furthermore, the heating value, melting point, cetane number, viscosity and oxidation stability decrease whereas density, bulk modulus, fuel lubricity and iodine value increase as the degree of unsaturation increases. McCormick et al. [58] investigated the impact of biodiesel chemical structure on NO_x emissions; specifically fatty acid chain length and number of double bonds, and found that NO_x increases with an increasing number of double bonds of the fuel, which can be quantified as the iodine value. McCormick et al. [104] studied various biodiesel with different degrees of unsaturation and reported that progressively increasing NO_x emissions due to the use of biodiesel fuels with higher degrees of unsaturation, which correlates with higher T_{ad}. Ban-Weiss et al. [29] investigated numerically to show the biodiesel NO_x effect and found enhanced the NO_x emissions of about 21% due to higher peak flame temperature of the double bonded methyl trans-2-butanoate about 14 °K than the single-bonded methyl butanoate. Pattamaprom et al. [105] analyzed the performance and emissions using palm olein and palm stearin (co-products of palm oil refining processes) biodiesel fuels and reported that palm olein has a slightly higher degree of unsaturation than palm stearin, which leads to a lower cetane number and

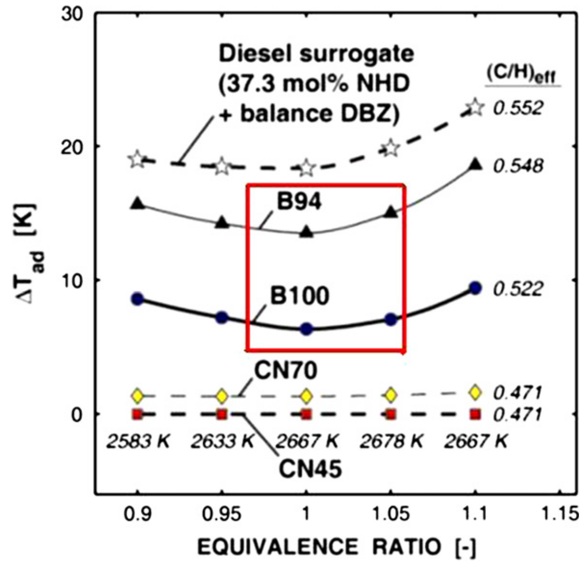


Fig. 4. T_{ad} difference relative to CN45 ($\Delta T_{ad}=T_{ad}$, fuel$-T_{ad}$, CN45), for near stoichiometric mixtures of B100, B94, CN45, CN70, and a diesel surrogate fuel with air [67].

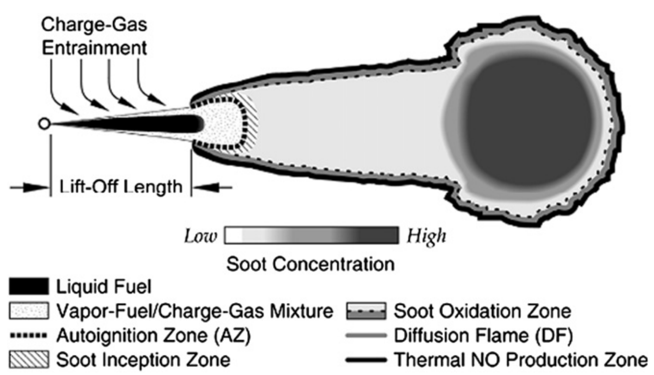


Fig. 5. Schematic of a reacting DI diesel jet during the quasi-steady period of combustion (Adapted from [67]).

thus, a higher combustion temperature, which implies greater NO_x formation.

In contrast point of view, Mueller et al. [67] presented an argument about the dependability of NO_x increasing of biodiesel on T_{ad}. From Fig. 4, the authors reported that T_{ad} for biodiesel is lower than that for diesel surrogate fuels, as well as higher than CN70 and CN45. If differences of T_{ad} were the NO_x controlling factor, then it could be surmised from Fig. 4 that biodiesel fuels would have lower NO_x than diesel; B94 would always have significantly higher NO_x than B100; and CN70 would have higher NO_x than CN45, but this was contradictory to other work in the literature. Zhang and Boehman [85] argued that having double bonds in biodiesel leads to the formation of free radicals that advances prompt NO_x. The linear chain of the unsaturated fatty acid decreases due to the presence of double bonds in the molecules, leaving less space for the molecules to compress together and hence, reduces compressibility [28,60].

3.5. Premixed-burn fraction

Because of having oxygen into biodiesel, it premixes more fully during the ignition delay, and a larger fraction of its heat release occurs during the premixed-burn phase of combustion at ignition. The combustion that is more premixes has higher oxygen concentrations and therefore produces more NO_x. The difference in NO_x produced during the premixed burn is responsible for the biodiesel NO_x increase.

3.6. Chemical kinetics effect

There are differences in the chemical-kinetic pathways that form NO_x when fuel is used as biodiesel, and these are responsible for the biodiesel NO_x increase. Arguments based on differences in prompt NO formation seem to be the most common in this category. Such arguments typically depend on increased levels of CH being produced at the AZ shown in Fig. 5 during biodiesel combustion [106]. These level leads to the production of N-atoms in the jet core followed by prompt NO formation once the mixture is convected to the DF where oxygen and OH are present.

3.7. Hydrogen addition into the combustion chamber

Tsolakis et al. [107] carried out an experiment to observe the effects of addition small amount of hydrogen to the engine intake with or without EGR in diesel engine fuelled with 20% ROME. They concluded that addition of H_2 into the combustion chamber through the engine intake reduces both NO_x and smoke simultaneously. This is attributed to the hydrocarbon fuel replacement by hydrogen resulting from the addition of hydrogen and the subsequent reduction hydrocarbon fuel flow into the engine. The use of a small amount of hydrogen gave longer ignition delay (retard) by 2°CA, but the combustion duration was faster by about 5% when compared to ULSD and B20 operation without hydrogen. At the same time, the engine efficiency and the combustion quality were not affected adversely.

3.8. Ignition delay time

The time between the injection start and onset of combustion is called the ignition delay time. Ban-Weiss et al. [29] reported that in a combustion chamber, the reactants are rapidly preheated due to a longer ignition delay time, which results in an increase of the flame temperature and corresponding NO_x emissions. Benjumea et al. [93] reported that biodiesel fuels, having higher degree of unsaturation have longer ignition delay time which results in higher T_{ad}. Therefore, NO_x emissions increase according to the thermal NO_x mechanism. But in general case, the ignition delay of

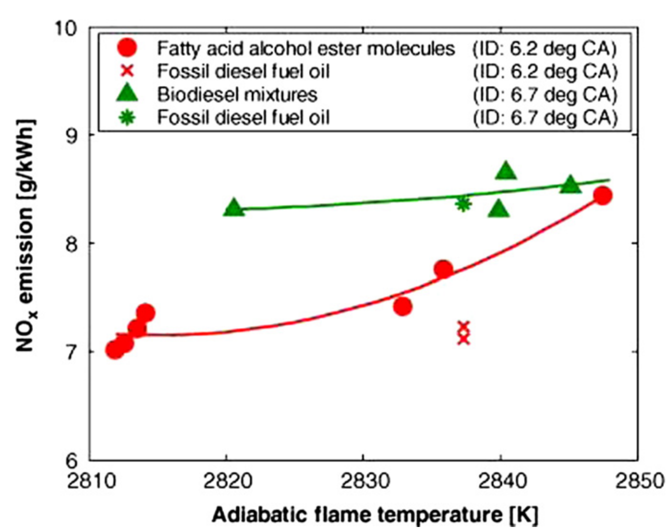


Fig. 6. Relationship between measured NO_x emission and calculated T_{ad} at $P=C$, $\Phi=1$, with no dissociation; Tin=881 K and Pin=4.5 MPa. Engine running condition as �=1200 rev/min, IMEP=0.4 MPa; ignition delay equalized to 6.2°CA for all fatty acid mono alkyl molecules [96].

Table 5
Effect of advance injection timing of biodiesel fuel compared to diesel fuel on NO_x emissions.

Engine specification	Fuel	Advance SOI timing	NO_x emission compared to diesel combustion	Reference
A John Deere diesel engine	Vegetable derived B100, B20	B100 (2.3°CA) B20 (0.25°) 0.75°CA	↑	[113]
A John Deere 4276T, Cyl: 4, 4S, TC, DI, diesel engine	Soybean biodiesel B100, B20	B100 (2.28° CA) B20 (0.4–0.6°) CA	B100 (10–24.5%)↑ B20 (0.62–16.6%)↑	[116]
Yanmar L70 EE, AC, 4S, Cyl: 1, DI diesel engine, maximum power output: 5.8 hp with high load (75%) and low load (25%) at 3600 rpm	soy-derived biodiesel	1.1°CA	↑ 6–9%	[118]
Lombardini 6 LD 400, Cyl:1, IOP: 20 MPa, SOI timing: 20 (deg CA BTDC), CR: 18:1, maximum torque: 21 N/m at 2200 rpm, maximum power: 8 kW at 3600 rpm	(COME+diesel)	5°CA	B5 ↑3.03%, B20 ↑8.6%, B50 ↑9.14, B100↑12.92	[121]

Note: AC=Air Cooled, NS=Number of stroke, Cyl.=number of cylinder, CA=crank angle, TC=turbocharged.

biodiesel is shorter than that for conventional diesel fuel at all load condition investigated by many researchers [10,96,97,108–112]. They reported that the contribution of some fuel properties of biodiesel, such as; the high cetane number, high ignition quality, increased chain length and degree of unsaturation etc., advance the combustion timing lead to shorter ignition delay and consequently, higher NO_x formation. Schönborn et al. [96] investigated the effect of molecular structure of natural biodiesel (NB) and single molecule fatty acid esters (SMFAE) on the combustion behavior under diesel engine conditions. They reported that for a shorter ignition delay time, the relationship between NO_x emissions and the T_{ad} becomes gradually steeper. This means that the influence of T_{ad} on total NO_x emissions is stronger, which is shown in Fig. 6. The T_{ad} plays an important role in forming NO_x because of the higher ignition quality of biodiesel fuel.

3.9. Injection timing (IT)

In combustion systems, injection timing is also an important parameter that affects combustion temperature and hence NO_x emissions. The start of fuel injection is advanced for biodiesel compared with petroleum diesel in rotary/distributor-style fuel injection systems, which has been reported by several authors [29,60,109,113–116]. Monyem et al. [113] carried out an experiment with a diesel engine fuelled by biodiesel without changing the setting of the injection timing and observed that B100 and B20 fuel injects about 2.3° and 0.25–0.75° earlier, respectively, than the studied petroleum diesel fuel. This injection timing advance can be attributed due to several properties of biodiesel e.g. high density, higher bulk modulus of compressibility, and greater speed of sound [96,117]. The higher bulk density and viscosity move the pressure wave inside the fuel pipe lines more quickly and an earlier needle lift results in advanced injection. Szybist et al. [118] studied injection and combustion processes of soy-derived biodiesel blends and Fischer–Tropsch (FT) diesel fuel. Their results showed that soy-derived biodiesel blends produced advance SOI timing of about 1.1° crank angle relative to diesel fuel because of the lower compressibility (higher bulk modulus). From the information in Table 5, it can be seen that increasing NO_x emissions with biodiesel is mainly caused by the advancement of injection timing, which has also been described by other researchers [117,119,120]. Injection timing advance generally lengthens the ignition delay; this permits additional time for premixing the fuel and air, which normally increases the premix portion of diesel combustion that increases the reaction temperature. Finally, it reaches an elevated diffusion reaction temperature to post-flame gas temperature. An increase in post-flame gas temperature

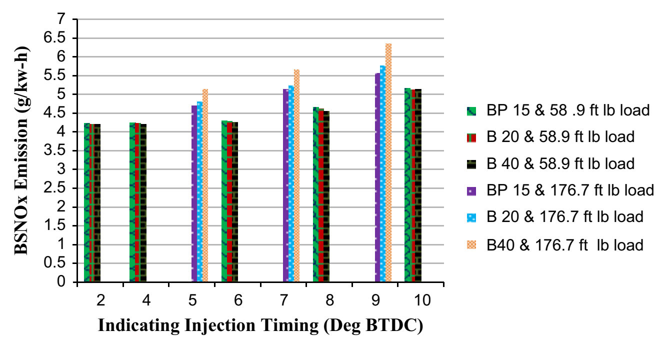


Fig. 7. Brake specific NO_x emission with respect single injection both high and low loads condition at 1600 rpm engine speed [85].

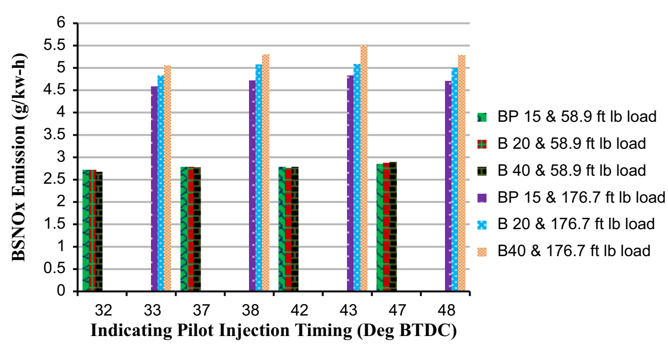


Fig. 8. Brake specific NO_x emissions with respect double injection both high and low loads condition at 1600 rpm engine speed [85].

enhances the NO_x formation rate. An advance of injection timing also typically progresses the onset of combustion, which can increase the reaction time and generally increase the overall gas temperatures [10,115,118].

3.10. Engine load condition

The variation of engine load has the greatest effect on combustion temperature and exhaust emission. Sze et al. [122] reported that the change in NO_x emissions increases linearly with the average cycle load. Zang and Boehman [85] investigated both low and high load conditions in order to detect the effect of the three fuels, named ultra-low sulfur diesel fuel (BP15), B20 (20% biodiesel into BP15), and B40 (40% biodiesel into BP15) on NO_x

emissions. Their results indicated slightly less NO_x emissions under low loads and obviously more NO_x emissions under high load conditions for biodiesel compared to baseline diesel fuel which is shown in Fig. 7. Fig. 8 shows that using pilot double injection at low load condition reduced the NO_x emissions greatly compared to high load condition by reducing the combustion peak temperature. Yoon and Lee [123] also agreed with this finding. However, they also found that significantly lower NO_x emissions emitted under dual-fuel (biogas–diesel and biogas–biodiesel) operation for both cases of pilot fuels compared to single-fuel mode at all engine load conditions. Another finding from their experiment was that the combination of ULSD and biogas produces less NO_x than biodiesel and biogas combination at any load condition. The main reason for this is that biodiesel has faster injection and early ignition characteristics that contribute to reaching a higher combustion pressure and temperature, promoting thermal NO_x emissions. Eckerle et al. [124] also reported after making combination with experimental and modeling work that the NO_x effect of biodiesel varied significantly with load. Under high load conditions, where diffusion flame combustion process dominates, it was shown that engine control parameters had a more significant influence on biodiesel's NO_x increase. On the other hand under low load conditions with more premixed combustion, others factors were more influential.

4. Reduction of the NO_x emissions

NO_x reduction techniques can broadly be classified into two groups as: pre combustion treatment techniques and post combustion treatment techniques. To meet the stringent vehicular exhaust emission norms worldwide, several pre and post combustion treatment techniques have been employed in modern engines. Both NO_x reduction techniques are discussed in this section.

4.1. Pre combustion treatment techniques

Use of different additives into fuel, exhaust gas recirculation (EGR), water injection, water fuel emulsion and retardation of injection timing are the common pre combustion treatment techniques to reduce NO_x emissions.

4.1.1. Use of different additives

Different types of additives such as metal-based, oxygenated fuel (dimethyl ether, ethanol, and methanol), diesel–vegetable oil blends, antioxidant, cetane number improver etc. are generally used to reduce the NO_x emissions form biodiesel combustion. By using ethanol into biodiesel as an additives reduces the NO_x emissions because of its having lower heating value [125]. The cetane number improver is used to reduce the biodiesel NO_x emissions by decreasing engine ignition delay and premixed combustion phase which implies to burn less fuel during the premixed combustion phase [62]. The maximum combustion temperature would be decreased, which suppresses the NO_x formation. However some effective cetane improvers such as 2-ethylhexyl nitrate (EHN), di-*t*-butyl peroxide (DTBP) are mostly used in biodiesel to reduce the NO_x emissions [23,30]. On other hand McCormick et al. [104] found addition of EHN as a cetane improver into 20% soy based biodiesel did not show any measurable effect to reduce the NO_x emissions. Antioxidant additives can be reduced the formation of free radical by four methods; chelating the transition metal catalysts, chain breaking reactions, reducing the concentration of reactive radicals and scavenging the initiating radicals and corresponding reduction of prompt NO_x [126]. Many researchers [127,128] reported on the effects of additives and catalysts on combustion, performance, and emission characteristics for biodiesel; the conclusions were that additives can improve the combustion characteristics. Table 6 presents a summary of NO_x reduction results by using different additives with various biodiesel fuels. From this table it can be observed that, additives e.g. 1% of ODA antioxidant, Mn, Ni, Mg, Co, (DGMME+DGMBE), 20% ethanol, 5% diethyl ether etc. can reduce NO_x emissions with a decrease in the CO and smoke range 13–64.28% and 16.67–30.91%, respectively compared to fuel without additives. Antioxidant *p*-phenylenediamine in biodiesel can reduce NO_x emissions by 43.55% compared to pure JME, but it increases the CO and HC emissions. On the other hand, 12 μ/moles Mg in 10% chicken fat biodiesel increases NO_x emissions by about 5%, but it decreases CO and HC emissions.

4.1.2. Exhaust gas recirculation (EGR) method

Exhaust gas recirculation (EGR) is a pre-treatment technique, which is being used widely to reduce the NO_x emissions from diesel engines by controlling oxygen density and combustion peak temperature [136,137]. The EGR mechanism decreases the combustion gas temperature, which is normally acceptable without any dilution effect and an inert gas effect with a higher specific

Table 6
Results of NO_x reduction by using different additives.

Test fuel	Additives	Engine condition	Results	References
POME20	1% of ODA	IDI,4C, 50 N/m load, @2250 rpm	NO_x↓22.69%, CO↓, HC↓	[129]
TOME60	Mn and Ni	Unmodified DI DE at full load	NO_x reduction rate for (TOME60Ni › TOME60Mn), CO↓ (64.28%), Smoke↓ (30.91%).	[130]
TOME60	Mg and Mo	1C, DI, DE at full load and speed vary	CO↓ (56.42%) and Smoke↓ (30.43%). Low NO_x emissions measured at (B60-8Mg and B60-12Mg) fuel.	[131]
POME	DGMME and DGMBE	1C, Kirloskar AV-I engine.	Reduced the NO_x emissions.	[132]
TOME60	Cobalt (Co)	1C, DI DE at full load and speed vary	CO↓ (53.37%) and Smoke↓ (29.47%). Measured low NO_x emissions at T60-8Co	[77]
10% chicken fat biodiesel	12 μ/mole Mg	4S,1C,AC,DI,Diesel engine,	CO↓13%, smoke↓9%, SFC↑5.2%, NO_x↑5%	[133]
SOME80	20% ethanol	1C, 4S, DI DE	NO_x↓ 12%, CO↓ 16.67%, CO_2↓ 18.75%,SO_2 ↓52%	[134]
JME	Antioxidant *p*-phenylenediamin	1C, 4S, WC, DE, 4.4 kW power.	NO_x emissions↓43.55% but↑(CO & HC) compare to pure Biodiesel.	[27]
B30	BE-1 (5% diethyl ether with B25) BE-2 (5% ethanol with B25)	1C, 4S, DI engine DE @ 2000 r/min.	The serial of NO_x reduction rate higher to lower (BE-1› B30› BE-2).	[135]

Note: DE=diesel engine, DI=direct injection, DGMME=diethylene glycol mono methyl ether, DGMBE=diethylene glycol mono butyl ether, ODA=octylated diphenylamine antioxide.

Table 7
The result of reduction NO_x emissions by using EGR method for petroleum and biodiesel blends fuel.

References	Engine used	Fuel used	EGR condition	Results	Explanation
[142]	1C, DI diesel engine.	Diesel	Cold start OEV (0,50,100) OCV (100,50,10)	NO_x↓ 60% at 100% OCV and 100% OEV	Less common rail pressure fluctuation and stable combustion
[147]	6C, TC, Volvo-(D-12)	Diesel	12% EGR	NO_x↓65.2%,BSFC↑ 8.6%	–
[143]	4S, 1C, (DI) diesel engine at HCCI condition.	LPG+ Diethyl ether (DEE)	At full load condition, 20% EGR	NO_x↓68% at full load & BTE↑ 2.5% at partial load	Lower the peak elevated temperature
[148]	1C, vertical, 4S, HCCI diesel engine	Diesel+ H_2 (.15 kg/h)	20% EGR at 80% engine load	NO_x↓ 41.4%, smoke↓ 8.3%, CO_2↓29.1% HC↓12.3%, BTE↑ 2% compared to neat diesel	Reduction the combustion peak temperature causes of inert gas of EGR
[145]	1C, DI, 4S, WC, diesel engine.	JME	Hot EGR levels of 5–25% at full load	NO_x↓7.7% at 15% EGR(optimum) compare to diesel fuel with same % of EGR	Sufficient NO_x reduction and minimum possible HC, CO, smoke and sensible BTE
[140]	2C,4S, WC, DI diesel engine	JOME	Optimum EGR rate 12% at FL	NO_x↓33%,BSFC↑11%	↓ in-cylinder maximum temperature due to↓O_2 density
[149]	2C, vertical DI, WC, diesel engine.	B20 (20% SOME+ 80% diesel)	15% EGR rate	NO_x↓ 25% HC↓ 5% CO↓ 10% smoke↑ little	Less flame temperatures due to few O_2 available in the recirculating exhaust gas.
[136]	4C, WC, TC, IDI diesel engine	20% JME biodiesel	10% EGR rate	NO_x↓36% Smoke ↓31%,	Limited EGR rate of 5–15%, with small effects on engine performance
[150]	4C, 16 valve Mercedes	SME100	27% EGR, Load=68 N/m	NO_x ↓87.7, CO↑, CO_2↑5.5, PM↑	–

Note: DI=direct injection, IDI=indirect injection, HCCI=homogeneous charge ignition engine, WC=water cooled.

Table 8
Result observation the reduction of NO_x by using a water injection method.

Engine specification	Fuel used	Injection condition	Results				References
			NO_x	CO	BSFC	BTE	
6C, TC Volvo-(D-12)	Diesel	30% H_2O	↓42%		↑ 2.1%		[147]
2.0 L WC, HSDI diesel engine	Diesel	M_w=60–65% of the fuel	↓50%	↑	↑	↓	[151]
Kirloskar, TAF1, 4S, AC, CI engine, Cyl: 1, CR: 17.5:1, IT: 23° BTDC, rated power: 6 BHP at 1500 rpm	Diesel fuel+H_2O (1:0.4)	–	↓37.62%	↑	–	–	[156]
4C, 4S, DI, TC, diesel engine	ROME	Flow rate: 3 kg/h & 1.8 kg/h	↓50% at 3 kg/h & ↓30% at 1.8 kg/h	↑ at both flow rate	Max ↑4% at at 3 kg/h	Max ↓3% at at 3 kg/h	[154]

Note: HSDI=high speed direct injection.

heat ratio, such as carbon dioxide and H_2O [138,139]. Both these molecules have higher heat capacity than air [140]. Here, the availability of the amount of oxygen in the intake mixture is low due to air displacement by recirculated exhaust gas. The effective air-fuel ratio is lower because of the reduction of oxygen for combustion, which affects exhaust emissions. The specific heat of intake mixture increases after a mix up between the recirculated exhaust gas and intake air, which results in the reduction of the flame temperature because more energy is needed to preheat the incoming mixture [137]. As a result, the combined effect of lower amounts of oxygen in the intake air and the reduction of the flame temperature reduces the NO_x formation rate [137,141]. Some researchers [142–145] investigated the effect of EGR on an engine fueled with diesel, biodiesel and gasoline, which proved the effectiveness of the EGR method as a part of NO_x reduction technology. Tsolakis et al. [146] investigated the effect of EGR on engine performance and emission for a diesel engine operated with ROME and ULSD blended fuels. The authors observed that the use of 20% EGR was more effective and achieved a reduction of about 10% and 30% at 4.5 bar IMEP for B50 and B100, respectively, with 3° CA retardation in IT. However, at 6.1 bar IMEP NO_x reduction was about 20% for both B50 and B100 without significant effect on fuel consumption and engine efficiency. Entering more H_2O vapor and CO_2 into the combustion chamber due to the increase in SFC of biodiesel fuel, lowers the air/fuel ratio (λ) for biodiesel compared with the operation of ULSD fuel, which are vital for greater NO_x reduction using EGR. Table 7 presents the NO_x emissions reduction results by using the EGR method for petroleum and various biodiesel blended fuels. It is observed that for diesel fuel, a drastic NO_x reduction of about 41.4–65.2% at 12–20% EGR rate was obtained with decreasing HC, smoke and CO_2, but increasing BSFC compared with neat diesel combustion without EGR. On the other hand for various pure and blends of biodiesel fuels by using EGR rate (5–25%), the reduction of NO_x was about 25–75% with slight decreasing HC and CO emissions, but increasing BSFC and smoke emission. For 20% JME biodiesel at 10% EGR rate, both NO_x and smoke emission reduced by about 36% and 31%, respectively, which was positive at a time reduction of NO_x and smoke emissions.

4.1.3. *Water injection method*

Water injection (WI) into the combustion chamber is another important method for controlling NO_x emissions from internal combustion engines. There are two ways to inject water into a combustion chamber as: inlet water injection and water injection to combustion chamber directly [151]. Samec et al. [152] showed that an inlet water injection system, both multipoint WI in the intake pipes and single point WI upstream or downstream of the compressor produced in turbocharged engine the same reduction of NO_x emissions. Hountalas et al. [153] investigated the effect of both water-fuel emulsion (see next section) and water injection

into the intake manifold on reduction of NO_x emissions, through testing in direct injection heavy-duty diesel engines by varying the percentages of injected water. The outcome from their analysis of NO_x reduction technologies was that the water—fuel emulsion was better than water injection, but both were more efficient than conventional diesel engine operation. However, direct water injection has an advantage over the water–diesel emulsion system, which is, it offers the possibility to change the water-to-fuel ratio during changes of the parameters of the engine [151]. Tesfa et al. [154] experimented with the effect of water injection on engine performance and emission characteristics for a direct injection (DI) turbocharged diesel engine fuelled with ROME. They concluded that water injection in the intake manifold did not show any important variation of the peak cylinder pressure and heat release rate of the bio-fueled engine, but that it does affect the premixed combustion temperature, which is the main factor for NO_x emissions. From the data in Table 8, it is found that the water injection method reduces NO_x emissions by up to 50% for both diesel and biodiesel fuelled engines with a slight increase in CO and BSFC, as well as a decrease in BTE. Recently, Adnan et al. [155] studied the influence of variable water injection timing on the performance and emission analysis fueled with hydrogen in a compression ignition engine. In their experimental setup, water was injected from 20°BTDC to 20°ATDC for the injection duration of 20°CA and 40°CA. They concluded that the lowest NO_x emissions were observed in the water injection timing of 0°CA and duration of 40°CA, but that this produced the highest O_2 and SO_2 emissions.

4.1.4. Water—fuel emulsion method

The use of the emulsification method is motivated by both cost reduction and the potentially effective techniques for reducing exhaust emissions from diesel engines. Water/diesel (W/D) emulsified formulations are mainly used to reduce the emissions of NOx, SO_x, CO, and particulate matter (PM) without decreasing the engine's performance. The water–diesel emulsion method is used to reduce the local T_{ad} by vaporizing the water, taking heat from the combustion chamber, which results in a reduction of NO_x emissions [157]. Tran and Ghojel [158] also reported that water diesel emulsion (WDE) and direct water injection (DWI) are two effective methods effective for introducing water into diesel engine combustion chambers to reduce NO_x emissions by lowering the flame temperature. Introduced water particles convert into steam due to the high pressure and temperature inside the combustion chamber at compression stroke, removes some heat from the engine cylinder to fulfill the latent heat requirement. Table 9 shows the effect of water emulsion with fuel on exhaust emission and the T_{ad} and it is found that the water–diesel emulsion process decreases the NO_x about 9–60% compared to neat diesel under low speed conditions. However, most authors [156,159–162] found this process increases the HC and CO emissions, except some researchers [79,162] who experimented under low and partial load conditions. It is also observed that by water–diesel emulsion, the fuel decreases the T_{ad} by about 15–26 °K compared with the base fuel [78,79]. Water biodiesel emulsion fuels also give a slight decrease in NO_x relative to biodiesel and diesel fuels without emulsion. Subramanian [156] also investigated experimentally a comparative analysis between water-fuel emulsion and timed injection of water into the intake manifold of a diesel engine, to establish the best solution for the reduction of NO_x and smoke emissions. The experimental results indicated that both NO_x reduction technologies reduced NO_x emissions by about 37% compared to baseline diesel, but the controlling capacity of smoke emission for water-fuel emulsion was more than water injection. After a huge comparative study, the author suggested

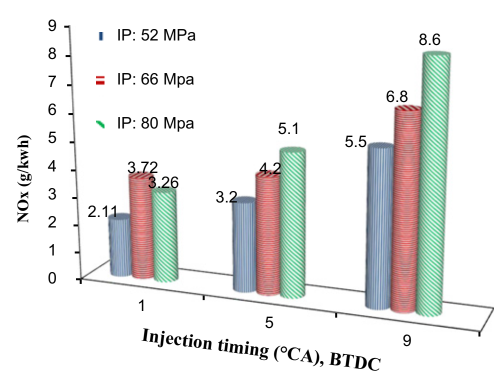


Fig. 9. Results of NO_x emissions for different injection timing and pressure at 25% load for SME40 fuel [173].

Table 9
Different experimental result of effect of water-fuel emulsion on exhaust emissions.

Emulsion	Engine and test condition	NO_x	Other emissions	T_{ad}/BSFC/BTE	Reference
Water emulsified diesel	4 cycle, WC, 6C, 121 kW; LS‹ 1000 rpm. HS› 1400 rpm	↓9.5% at LS & ↓29% at HS with ↑(W/O)	(HC, CO, smoke)↑ with emulsion ratio (W/O)↑	Minor BSFC↑ at LS but BSFC↓2.6% at HS	[159]
Water–diesel emulsion: 20%+EGR; 16.7%	4C, DI, Ford diesel engine.	↓ up to 60%	HC↑, smoke↓, CO↑	BSFC & BTE not change	[160]
Water–oil emulsified	IID, TC, DE, speed: 2087–3175 rpm	↓	THC↓	T_{ad}↓ about 26 K, BTE↑ slightly,	[78]
Diesel +GS/CS+5–15% water	XLD418 type DE of Ford,4S, 4C, WC; speed: 1000–5000 rpm	↓ (high) at GS (15% W)	CO↓compare to neat diesel, PM↓ (68–72%)	T_{ad}↓ about (15–25)K, BSFC↑	[79]
Water–diesel emulsion (0.4:1)	4S, AC, 1C, CI engine; CS: 1500 rpm	↓37.6%	HC↑, CO↑	BTE↓ at LL &↑at FL	[156]
94%D+ 5%H_2O+0.5% tween 20+0.5% span 20	Comet DE, 2C, Vertical WC, 7.5 kW; 1500 speed	↓(30–50)%	HC↓ at LL but↑at HL, CO↑ with↑H_2O emulsion	–	[161]
D78.5%+10%H_2O+ additives 11.5%	Toyota, 4C, 4S, DE; speed: 1000–4000 rpm	↓30.6%	(HC↓, CO↑) at partial load, but (HC↑, CO↓) at FL	BTE↑ 14.2%	[162]
10% CH_3OH+ cooking biodiesel	4C, DI, DE; speed:1800 rpm speed & 5 types of load	↓6.2%	–	BTE↑ at LL but↓at HL	[163]
Biodiesel, diesel, B70D10E20M micro emulsion fuel	1C, WC, DI, diesel engine; CS: 1500 rpm	Emission of NO_x less than (diesel, BD)	(BD‹ Micro emulsion fuel‹ Diesel) for HC & smoke; (BD‹ B70D10E20M‹ Diesel) for CO	BSFC↑ but BTE not vary compare to diesel fuel.	[164]
H_2O-BD-diesel Nano emulsion	Diesel engine	↓	CO↑	–	[165]

Note: AC=air cooled, WC=water cooled, HS=high speed, LS=low speed, IID=intercooler indirect injection, GS=Gemini surfactants, CS=conventional surfactants, BSFC=brake specific fuel consumption, BTE=brake thermal efficiency.

that the emulsion method is more efficient than the injection method in reducing both NO_x and smoke emissions at all loads.

4.1.5. Retardation of injection timing

A slight control on the injection timing by retarding it can reduce the NO_x emissions significantly [67,104,110,113,166–170]. Graboski and McCormick [70] reported in their review paper which published in 1998 that using biodiesel in both 2-stroke and 4-stroke diesel engines increased NO_x emissions, but that these increases could be effectively controlled by retarding the fuel injection timing by 1–4°. Later on, Choi and Reitz [171] indicated that for both retarded and split injection techniques reduced the amount of premixed burning, thereby reducing in-cylinder temperatures and found beneficial effect on NO_x reduction. Kegl [172] demonstrated that biodiesel could produce lower NO_x emissions compared to diesel, if the injection timing was retarded. Sayin et al. [121] investigated the effect of both advancing and retarding the SOI on exhaust emissions from diesel engines fuelled with CME blends. The authors concluded that advancing the SOI gave the best results for smoke and CO emissions for B100, whereas retardation of the SOI presented the minimum results for NO_x and CO_2 emissions for both B0 and B100 fuels. Wang et al. [169] investigated NO_x formation for diesel and biodiesel in a light-duty compression ignition engine by using computational fluid dynamics (CFD) and finally concluded that retarded fuel injection timing is an effective method for reducing NO_x emissions because of the retarded combustion phasing (lower temperature). The retardation of SOI timing decreases NO_x emissions because late combustion implies a reduction of effective pressure. Recently Ye et al. [173] observed that NO_x emissions for SME40 fuelled engine reduced by retarding the IT whereas increased with increasing injection pressure (IP) which is shown in Fig. 9. By applying this method, it reduces the reaction time by the late onset of combustion, which can decrease the overall gas temperature. However, retarded injection timing also reduces the brake thermal efficiency and increases the smoke emission, which is summarized by Rajasekar et al. [24]. Some experimental results are shown in Table 10 about the effect of retarding the SOI timing, where each result represents a reduction of NO_x by 8.2–40.95% compared with the original SOI timing, but an increase in HC and CO emissions, except for the experiments of Mani and Nagarajan [174] and Kegl

Table 10
Effect of retard injection timing of biodiesel and diesel fuel compared to original injection timing on NO_x emissions.

Engine specification	Retard the SOI timing	Fuel types	Emissions result			*Sources*
			NO_x	CO	HC	
Ricardo E6-MS/128/76, 1C	4°CA from ORG 38°CA BTDC	Diesel	↓40%	–	–	[175]
Super star 7710, 1C,4S, DI	6°CA from ORG 27°CA BTDC	E5+D95	↓37.3	↑	↑	[176]
Ford 6.0 lt. T/C LHR, TC, 6C, DI,	(2–4°)CA from ORG 20° CA BTDC	Diesel	↓11%	–	–	[167]
A John Deere diesel engine	3° CA retarded injection timing	Vegetable derived B100, B20	↓(35–43)%	–	–	[113]
Diesel engine	Retard SOI timing from ORG	Pongamia oil methyl ester (PME)	↓	↓	↓	[110]
MAN D 2566 MUM, 4S, 6C, WC	4°CA from ORG 23°CA BTDC	ROME100 compared to diesel fuel	↓25%	↓25%	↓30%	[172]
Kirloskar TAF1 1C, 4S, DI, AC	9°, 6°, 3°CA from ORG 23°CA BTDC	Waste plastic oil	↓	↓25%	↓30%	[174]
Small power DE	Retarded SOI	KOME	↓8.2%			[177]
Lombardini 6 LD 400, Cyl:1, IOP: 20 MPa, SOI timing: 20 (deg CA BTDC), CR: 18:1, maximum torque: 21 N/m at 2200 rpm, maximum power: 8 kW at 3600 rpm	5°CA from ORG 20°CA BTDC	(CME+ Diesel), Fuel blends: B0, B5, B20, and B50 & B100.	B0↓40.95, B5↓30, B20↓28, B50↓15.59 & B100↓9.77	B0↑13.21, B5↑11.39, B20↑21.08, B50↑31.25 & B100↑35.11	B0↑13.54, B5↑9.1, B20↑33.3, B50↑27.03 & B100↑44.68	[121]

Note: LHR=low heat rejection, TC=turbocharged, DI=direct injection, AC=air cooled.

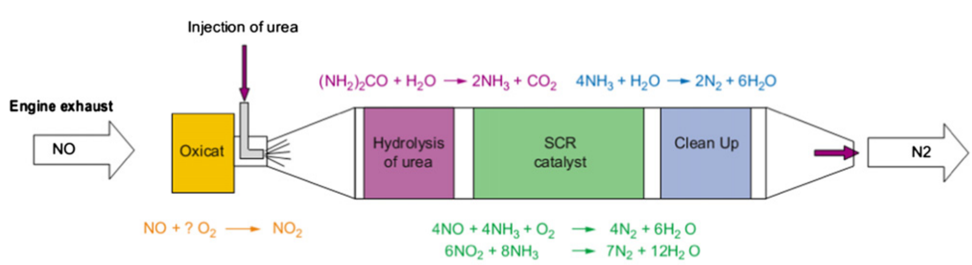


Fig. 10. Schematic view of SCR system [181].

[172]. Retardation of SOI timing also increases the BSFC with some exceptional such as [167,175].

4.2. Post combustion treatment techniques

A few research groups have performed experiments based on controlling the biodiesel NO_x in modern engines using advanced after-treatment systems. There are some commonly used after-treatment approaches to reduce the NO_x emissions from diesel engines such as NO_x adsorber catalyst (NAC), selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and $DeNO_x$ (Lean NO_x) catalysts. All of these approaches are considered to have good potential of meeting the US EPA emissions standard.

4.2.1. NO_x adsorber catalyst (NAC)

NO_x adsorber catalyst (NAC) is one of the significant NO_x reduction techniques which is also called as lean-NO_x trap system. It can be used in lean-burn gasoline and diesel engines to reduce NO_x emissions by a number of manufacturers. The working principle of the NO_x adsorber system is to store NO_x in a catalyst during periods of lean operation and then release the NO_x during rich condition of engine [178]. The excess unburned hydrocarbons react to reduce the NO_x emissions. In a NAC system utilizes an oxidation catalyst to exchange all NO to NO_2, which is then trapped in an inorganic substance such as barium oxide (BaO). During rich condition of engine, nitrate becomes unstable and decomposes which causes releasing of the stored NO_2. NAC systems are very sensitive to sulfur contamination because of forming of sulphur compounds to stable sulphates along with NO_x absorbing materials which reduces the performance of catalyst gradually. Ultra-low sulfur diesel (ULSD) or SO_x trap is now required to improve the effectiveness and durability of modern diesel emissions control systems. Tatur et al. [179] performed an experiment about biodiesel effects on US light-duty tier 2 engine and emission control using a NAC system. They found that the engine-out NO_x was somewhat higher for soy-based biodiesel (B20) compared to diesel combustion (by up to 10%), while tailpipe-out NO_x was slightly lower. The higher exhaust temperature of diesel combustion was the main contributor of higher tailpipe-out NO_x compared to B20. As a result, the NAC was more effective for biodiesel (B20) combustion to trap NO_x emissions than diesel combustion.

4.2.2. Selective catalytic reduction (SCR)

At stationary combustion installations, the selective catalytic reduction (SCR) has been used to reduce NO_x emissions for many years by ammonia (NH_3). With SCR, a different catalyst bed is used to convert the NO_x into water and nitrogen (N_2) directly [180]. However, separate injection system is required to inject the chemical reducing agent into the exhaust stream, ahead of the SCR catalyst. For vehicle applications, the reducing agent is not NH_3 but an aqueous solution of urea (NH_2CONH_2) [181]. The conversion mechanism of NO into N_2 is presented with the schematic view of the SCR system in Fig. 10. A greater issue concerning about an ammonia based SCR system is that using a slight excess of ammonia which produces "ammonia slip "emissions. But introducing slight excess of NH_3 is helpful to get the maximum reduction of NO_x emissions. McWilliam and Zimmermann [182] investigated the effect of biodiesel usage in a HD Caterpillar engine equipped with a vanadium-based SCR system. Author found that the NO_x conversion efficiency of the SCR system was reduced by 6% when operating on B100 because of reducing the NO_2/NO_x ratio substantially. This adversely affected the ammonia-driven reduction reactions within the SCR, and caused an increase in ammonia slip emissions. An additional oxidation catalyst may be used to overcome the ammonia slip emissions problem.

4.2.3. Selective non-catalytic reduction (SNCR)

Selective non-catalytic reduction is another method used to reduce NO_x emissions. This involves the injection of a NO_x-reducing agent, such as ammonia or urea, into the boiler exhaust gases at a temperature of approximately 760–870 °C in the absence of any catalyst. The ammonia or urea breaks down the NO_x in the exhaust gases into water and atmospheric nitrogen. The mechanism of NO_x reduction after treatment system as SNCR is shown in Fig. 11. It can be reduced NO_x emissions up to 70% [35]. Krahl et al. [183] reported on addition of amine compounds at relatively high concentrations (2–4%) to both conventional diesel and biodiesel fuels. Authors presented a strong argument that SNCR could reduce the NO_x emissions from diesel engine in an efficient way when proper compounds are chosen to do the work. However, the NO_x reduction approaches as SNCR has some restrictions to apply commercially due to amine solubility's and high cost.

4.2.4. $DeNO_x$ (Lean NO_x) catalysts

Application of $DeNO_x$ or "Lean NO_x" catalysts is another important NO_x reduction after-treatment system. These use the same operating principle as SCR but use hydrocarbons as the NO_x reductant instead of an ammonia solution [178]. The converting reaction of NO_x into N_2 by using $DeNO_x$ catalysts is presented in Eq. (12).

$$HC + NOx \rightarrow N_2 + CO_2 + H_2O \tag{12}$$

These catalysts can be divided into two groups: passive and active $DeNO_x$. Though the passive systems are simple, reliable and low cost, but their capacity is limited due to selective nature of the reaction and low concentration of HC in exhaust. On the other hand, enrichment of the exhaust gases with additional HC material has been perceived as a solution to this problem. In general, such enrichment could be realized by two methods: injection of HC preferably diesel fuel and later in-cylinder injection in a common rail fuel system. Catalysts with HC enrichment can overcome the problem of passive $DeNO_x$ system. $DeNO_x$ or "Lean NO_x" catalysts

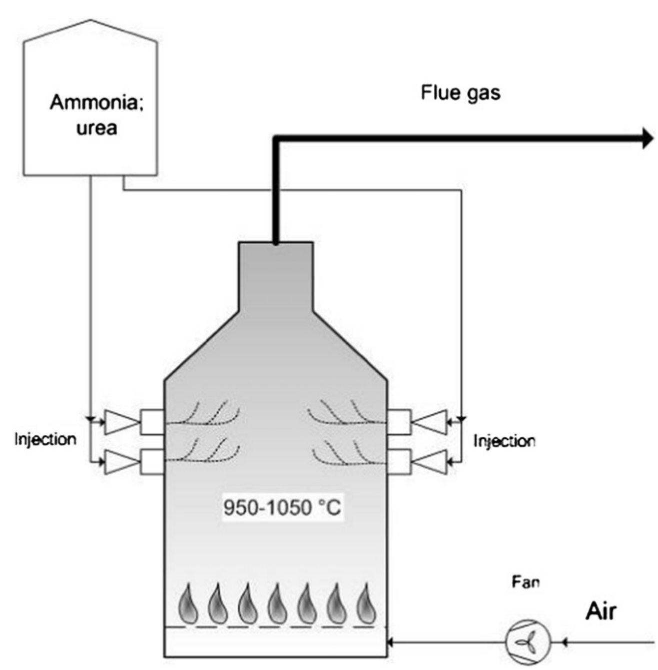


Fig. 11. Selective no catalytic reduction (SNCR) process [35].

convert to a significant fraction of NO_x to N_2O which is a potent greenhouse gas.

5. Summary and conclusion

Biodiesel, produced from renewable and often domestic sources, is a more sustainable source of energy and will therefore play an increasingly significant role in meeting energy demands. Therefore, research on the different feedstock and their influence on performance and emissions are increasing progressively. However NO_x emissions from biodiesel fuelled engine is the major concern of the researchers. The effects of different notable factors on NO_x emissions in biodiesel fuelled engine and its reduction approaches (both pre and post combustion) have been investigated in this work. The effective NO_x reduction approaches are retarded injection timing and EGR system which are able to overcome the problems of biodiesel NO_x effect. However, the following conclusions could be drawn from the analysis of the related literatures in this article:

1. In general, thermal NO_x is a dominant mechanism in the combustion processes; however, prompt NO_x also contributes significantly in biodiesel combustion.
2. The presence of oxygen in biodiesel fuel results in higher heat release during the premixed phase combustion which can be regarded as the main contributor to increased NO_x emissions. However less NO_x emissions for oxygenated fuels were also observed by few researchers.
3. Biodiesel has a high cetane number that implies shorter ignition delay and reduction of NO_x emissions is expected. However elevated combustion temperatures reached during the combustion process due to advanced combustion timing and longer residence period, increase NO_x emissions.
4. Physicochemical properties of biodiesel such as: Viscosities, density, bulk modulus of compressibility, iodine value, surface tension are higher than diesel that influences biodiesel NO_x effect.
5. Higher adiabatic flame temperature may be one of the reasons for biodiesel NO_x emissions; however, it could not be the exact reason. Degree of unsaturation of biodiesel fuel is the main responsible for the higher T_{ad}.
6. Biodiesel produces higher NO_x emissions with increasing engine load and vice versa. Addition of small amount H_2 into combustion chamber through engine intake can reduce the NO_x and smoke emissions simultaneously.
7. Addition of additives into biodiesel reduces the NO_x emissions effectively by improving fuel properties such as viscosity, density etc. However this poses engine operating cost and durability of engine.
8. The injection timing of biodiesel is advanced compared to neat diesel fuel due to higher density, high bulk modulus of compressibility, etc., which results in more NO_x emissions. By applying the retarded injection timing method, NO_x can be reduced by 8.2–40% relative to the original injection timing, but in most cases, this technology increases CO and HC emissions, as well as BSFC.
9. EGR is the method with the greatest potential for reducing NO_x emissions. It reduces NO_x emissions with biodiesel by about 25–75% at 5–25% EGR rate. It also decreases HC and CO emissions slightly, but raises the BSFC and smoke emission.
10. The water injection method reduces NO_x emissions by up to 50% for diesel and biodiesel fuelled engines. However it increased CO and BSFC slightly, as well as decreased BTE by reducing the premixed combustion temperature.
11. Water-fuel emulsions are more efficient for reducing NO_x emissions than the water injection method because of low cost, greater reduction of smoke, and reduction the local adiabatic flame temperature, etc. However they are inherently unstable and prone to phase separation, which may damage engine.
12. Applying exhaust after-treatment systems in biodiesel engine may be required to meet the progressively stringent diesel engine emissions standards. However increased GHG, higher engine operating cost, ammonia slip emissions etc. makes them unviable as long term solution.

Further studies are required to determine the effect of biodiesel combustion on NO_x formation by changing different engine parameters e.g. fuel injector, ignition timing and engine calibration (air/fuel ratios, injection pressure, injection timing, injection phasing). Furthermore, research on several new combustion technologies such as low temperature combustion (LTC), homogeneous charge compression ignition (HCCI), and premixed controlled compression ignition (PCCI) are also needed to control biodiesel NO_x emissions. Moreover, studies undertaking exhaust after-treatment systems for biodiesel fuelled engine is necessary for long term commercial use.

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